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(71) TRICAN WELL SERVICE LTD., 2700, 645 7th Ave. SW, CALGARY, A1 (CA).

(72) O'NEIL, BILL (CA).
ZHANG, KEWEI (CA).

(74) STIKEMAN, ELLIOTT

(54) FLUIDE DE FRACTURATION
(54) FRACTURING FLUID

(57)

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(71) Demandeur/Applicant:
TRICAN WELL SERVICE LTD., CA

(72) Inventeurs/Inventors:
ZHANG, KEWEI, CA;
O'NEIL, BILL, CA

(74) Agent: STIKEMAN, ELLIOTT

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(57) Abrégé/Abstract:
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ABSTRACT

A subterranean fracturing fluid includes an amphoteric surfactant, specifically a betaine surfactant and an alcohol in an aqueous medium. Depending upon the proportions of the ingredients, the fluid can be foamed.

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to a fracturing fluid and to a method of fracturing a subterranean formation to increase the permeability of the formation.

More specifically, the invention provides a viscoelastic surfactant based fracturing fluid for fracturing a subterranean formation and transporting proppant into thus created fractures.

DISCUSSION OF THE PRIOR ART

Hydraulic fracturing has been used for many years to stimulate the production of petroleum from subterranean formations. In hydraulic fracturing, a fracturing fluid is injected through a wellbore into the formation at a pressure and flow rate sufficient to overcome the overburden stress and to initiate a fracture in the formation. Frequently, a proppant, whose function is to prevent the created fractures from closing back down upon itself when the pressure is released, is suspended in the fracturing fluid for transport into a fracture. Proppants in use include, for example 20-40 mesh size sand and ceramics, but the most common proppant is sand. The proppant filled fractures provide permeable channels allowing petroleum to seep through the fractures into the wellbore from whence it is pumped to the surface. Accordingly, a desirable fracturing fluid should have the following properties: (a) to be compatible with the reservoir rock and reservoir fluids, (b) have sufficient viscosity and fluid structure to suspend proppants and transport them deep into the formation, (c) be stable enough to retain sufficient viscosity and fluid structure throughout proppant placement, (d) possess low fluid loss properties and low fluid flow friction pressures, (e) be easily

removed from the formation with little residues, (f) be easily made under field conditions and (g) be relatively inexpensive. Production of petroleum can be enhanced significantly by the use of specialized fracturing fluids, which exhibit high levels of rheological performance.

Fracturing fluids in common use include various aqueous gels and hydrocarbon gels. The gels are formed by introducing cross-linkable polymers or surfactants into an aqueous or hydrocarbon fluid, followed by cross-linking of the polymer or surfactant molecules. The cross-linking give the fluid high viscoelastic properties that are necessary to transport and place proppants into the fractures.

Another widely used fracturing fluid is a foamed, water-based fracturing fluid. Such a fluid is described, for example, in U.S. Patent No. 3,980,136, issued to R.A. Plummer et al on September 14, 1976. Briefly, the foamed fracturing process involves generation of foams with a desired quality which are pumped through a wellbore into a formation. Typically, for aqueous systems, a polymer has to be hydrated in water at the surface before being pumped into the formation. The process of polymer hydration is time consuming and often requires bulky equipment at the wellsite. Another problem common to polymer-based fracturing fluids is that a significant amount of polymer residue is left in the formation resulting in negative impact on formation permeability.

Viscoelastic surfactants have long been used for well stimulation. A surfactant is a type of substance, which contains both hydrophobic and hydrophilic groups in the same molecule. The hydrophobic group is usually one of a variety of alkyl groups and the hydrophilic group can be ionic, which may be positive (cationic), negative (anionic)

or contain both positive and negative moieties (amphoteric), or nonionic - often consisting of a neutral polyoxyalkylene group. When dissolved in an aqueous medium, surfactants generally form various aggregates called micelles above a critical micelle concentration (cmc). At low concentration of surfactant, the micelles usually are small and spherical. Under certain conditions and surfactant concentrations, however, the spherical micelles grow in size and/or change their shape resulting in the formation of long flexible micelles. Above a certain concentration the long flexible micelles can become entangled and exhibit strong viscoelastic behavior. Even though this feature has been observed in a number of systems containing nonionic and anionic surfactants, the effect is more pronounced in cationic surfactants, especially those containing an amine or quaternary ammonium group, in the presence of certain organic counterions such as, for example salicylate, benzonate and alkyl sulfonate. Viscoelastic surfactant fluids have been studied extensively in recent years and have found a wide variety of uses in many applications.

U.S. Patent No. 4,061,580, issued to R.W. Jahnke on December 6, 1977 discloses surfactant gelled fracturing and acidizing fluids suitable for well stimulation. The gelled fluids are prepared by adding certain amine salts to aqueous acid or salt solutions. The amine salts used as thickeners are prepared by merely mixing one equivalent of amine per equivalent of acid or, in the case of polybasic acids such as sulfuric and phosphoric acids, as little as one-half equivalent of amine per equivalent of acid may be used resulting in the formation of an acidic salt. The aqueous acid or salt solution can be gelled by the addition of the above-described salts. For example, 15% by weight of HCl can be gelled by the addition of a small amount, usual 3-10% by

weight and typically about 5% by weight of an amine or amine salt as described above. For fracturing fluids, aqueous solutions containing some inorganic salts can be gelled by the addition of 3-10% by weight, preferably about 5% by weight, of an amine salt described above.

U.S. Patent No. 4,163,727, issued to C.G. Inks on August 7, 1979 discloses an acidizing-gel composition which consists essentially of, for example, about 15% by weight of HCl, about 20% by weight of a suitable nonionic gel-forming surfactant containing oxyethylene and oxypropylene units, a corrosion inhibitor to the extent needed, and the balance water.

U.S. Patents Nos. 5,551,516, issued to W.D. Norman et al on September 3, 1996 and 5,964,295, issued to J.E. Brown et al on October 12, 1999 disclose a fracturing fluid composition comprising a quaternary ammonium salt, erucyl bis (2-hydroxyethyl) methyl ammonium chloride, an organic salt such as sodium salicylate, inorganic salts such as ammonium chloride and potassium chloride and water. The patents state that the fluid has good viscoelastic properties and is easily formulated and handled. Furthermore, no or very little residue is left in a formation after the completion of the fracturing process. It is worth noting, however, that cationic surfactants such as amine and quaternary ammonium salts usually degrade very slowly, both aerobically and anaerobically, and moreover are highly toxic to marine organisms. The combination of low biodegradability and high toxicity is a fundamental criterion for a product injurious to the environment. In addition, cationic surfactants tend to render the formation, especially sandstone formations, oil-wet by adsorbing on the surface of clays and sands. The alteration of the formation wettability often reduces the relative

permeability of petroleum leading to high water/petroleum ratio and low production rates. The strong adsorption of cationic surfactant on the clay and sands may also adversely affect fluid viscosity.

GENERAL DESCRIPTION OF THE INVENTION

Thus, there is a general demand for surfactants, which are less harmful to both the environment and to subterranean formations, but which have the same excellent ability as above-mentioned cationic surfactants to form viscoelastic surfactant based fracturing fluids. An object of the present invention is to meet this demand.

Another object of the present invention is to overcome the disadvantages inherent to existing fracturing fluids by providing a fracturing fluid having relatively good foaming capability and foam stability in a wide range of temperatures.

According to one aspect, the invention relates to a fracturing fluid comprising an aqueous medium, at least one betaine surfactant having a saturated or unsaturated alkyl or acyl group containing 14-24 carbon atoms and an alcohol having the general formula

$$R_3\text{-OH}$$

wherein R_3 is a hydrocarbon group with 6-24 carbon atoms.

According to a second aspect, the invention relates to a method of fracturing a subterranean formation comprising the step of injecting a fracturing fluid into the formation at a pressure sufficient to initiate fracturing, said fluid including an aqueous medium, at least one betaine surfactant having a saturated or unsaturated alkyl or acyl group containing 14-24 carbon atoms and at least one alcohol having the general formula

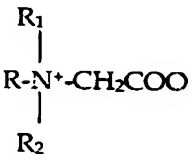
R_3-OH

wherein R_3 is a hydrocarbon with 6-24 carbon atoms.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As described above, the basic composition of the invention includes a betaine surfactant and an alcohol which are readily degradable. In addition, since betaine surfactants have strong foaming capability, the present composition also gives an excellent foaming capability and foam stability within a given temperature range, without employing additional foaming surfactants. The present fluid may also contain a gas, for example, N_2 or CO_2, and thereby be in the form of foams or energized fluids. In other words, the present fluid may also be utilized as a foamed water-based fracturing fluid in the presence of gas.

The betaine surfactant has a saturated or unsaturated alkyl or acyl group with 14-24 carbon atoms. The generally molecular structure of the betaine surfactant is represented by the general formula



where R is the alkyl group or the group $R'NHC_3H_6$, in which R' is an acyl group.

R_1 and R_2 are hydrocarbon aliphatic or aromatic, straight or branched, saturated or unsaturated groups and may also contain one or two hydrophilic moieties, such as hydroxyl(- OH), or ethoxy or propoxy moieties. The alcohol having the general structure

R_3- OH

where R_3 is a hydrocarbon group with 6-24 carbon atoms. The hydrocarbon group R_3 can be aliphatic or aromatic, straight or branched, saturated or unsaturated. The combination of the specific betaine surfactants and alcohols in an aqueous medium gives good viscoelastic properties within a given temperature range. The carbon numbers of the hydrocarbon groups R will determine the useful temperature range for a particular fluid so that high carbon numbers usually give products suitable for high temperatures.

The group R can suitably be tetradecyl, hexadecyl, octadecyl, oleyl, rape seed alkyl and tallow alkyl, erucyl, docosyl or the corresponding acyl group.

The preferred betaine surfactant is octadecyl dimethyl betaine. Alternative betaines may be employed either alone or in combination, including erucyl dimethyl betaine, docosyl dimethyl betaine, cetyl, dimethyl betaine, tallow dimethyl betaine, and myristyl dimethyl betaine. The preferred alcohol is benzyl alcohol. Alternatives include decanol, dodecanol and hexadecanol.

By "aqueous medium" is meant that at least 50% by weight, preferably at least 90% by weight, of the water-based liquid system consists of water. Within the term are plain water and aqueous solutions of inorganic salts and aqueous alkaline or acidic solution. Other exemplary aqueous liquids include mixtures of water and water-miscible liquids such as lower alkanols, e.g., methanol, ethanol or propanol, glycols and polyglycols. Also included are emulsions of immiscible liquids in the aqueous liquids, aqueous slurries of solid particulates such as sands, ceramics, or other minerals and a

number of conventional components such as clay stabilizers, antifreeze agents and bactericides. All of the additives, as well as the betaine surfactants, alcohols and water, are employed in amounts that do not deleteriously affect the viscoelastic properties of the fluid.

The present invention is described below in greater detail by means of the following examples.

EXAMPLES

The foaming properties of the compositions according to the present invention were tested by a simple method involving the measuring the viscosity of the gel.

Example 1

1.5 g active substance of octadecyl dimethyl betaine (in the following called C18 -betaine) was first dissolved in 200 ml of 5 wt% KCl aqueous solution. The resulting surfactant solution was mixed with 0.8g active substance of hexadecanol at 55°C. A clear gel with high elasticity was formed. The viscosity of the gel was measured using a Brookfield viscometer (Model LVT, Spindle 1 at 12 rpm) at 55°C. The results are listed in Table I.

Example 2

1.5 g active substance of C18 -betaine was first dissolved in 200 ml of 5 wt% KCl aqueous solution. The resulting surfactant solution was mixed with 0.6g active substance of tetradecanol at 40°C. A clear gel with high elasticity was formed. The

viscosity of the gel was measured using a Brookfield viscometer (Model LVT, Spindle 1 at 12 rpm) at 40°C. The results are listed in Table I.

Example 3

1.5 g active substance of C18 -betaine was first dissolved in 200 ml of 5 wt% KCl aqueous solution. The resulting surfactant solution was mixed with 0.2g active substance of decanol at 30°C. A clear gel with high elasticity was formed. The viscosity of the gel was measured using a Brookfield viscometer (Model LVT, Spindle 1 at 12 rpm) at 30°C. The results are shown in Table I.

Example 4

1.0 g active substance of C18 -betaine was first dissolved in 200 ml of 5 wt% KCl aqueous solution. The resulting surfactant solution was mixed with 0.5g active substance of benzyl alcohol at 22°C. A clear gel with high elasticity was formed. The viscosity of the gel was measured using a Brookfield viscometer (Model LVT, Spindle 1 at 12 rpm) at 22°C. The results are shown in Table I.

Example 5

1.5 g active substance of C16 -betaine was first dissolved in 200 ml of 5 wt% KCl aqueous solution. The resulting surfactant solution was mixed with 0.6g active substance of benzyl alcohol at 22 oC. A clear gel with high elasticity was formed. 22 °C. The viscosity of the gel was measured using a Brookfield viscometer (Model LVT, Spindle 1 at 12 rpm) at 22 °C. The results are shown in Table I.

Table I

Compositions			Viscosity of gels
1.	C18-Betaine Hexadecanol KCl	0.75% 0.4% 5.0%	340 cp
2.	C18-Betaine Tetradecanol KCl	0.75% 0.3% 5.0%	470 cp
3.	C18-Betaine Decanol KCl	0.75% 0.1% 5.0%	750cp
4.	C18-Betaine Benzyl alcohol KCl	0.5% 0.25% 5.0%	660 cp
5.	C16-Betaine Benzyl alcohol KCl	0.75% 0.3% 5.0%	220 cp

From the results of testing set out in Table I it is evident that combinations of a betaine surfactant and an alcohol in the aqueous medium form clear gels with good viscoelastic properties. These gels can be used for hydraulic fracturing applications. For applications requiring higher viscosity, higher surfactant loading is generally required. The present fluid may also contain a gas, for example, N2 or CO2, and thereby be in the form of foams or energized fluids. In other words, the present fluid may also be utilized as a foamed water-based fracturing fluid in the presence of gas

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A fracturing fluid comprising an aqueous medium, at least one betaine surfactant having a saturated or unsaturated alkyl or acyl group and at least one alcohol electrolyte having the general formula

$$R_3\text{-OH}$$

wherein R_3 is a hydrocarbon aliphatic or aromatic, straight or branched, saturated or unsaturated hydrocarbon group with 6-24 carbon atoms.

2. The fracturing fluid of claim 1,wherein the saturated or unsaturated alkyl or acyl groups contains 14 – 24 carbon atoms.

3. The fracturing fluid of claim 1 or 2, wherein the betaine surfactant has the general formula

$$\begin{array}{c} R_1 \\ | \\ R\text{-}N^{+}\text{-}CH_2COO^{-} \\ | \\ R_2 \end{array}$$

wherein R is an alkyl group or the group $R'NC_3H_6$ - wherein R' is an alkyl group, and R_1 and R_2 are hydrocarbon aliphatic or aromatic, straight or branched, saturated or unsaturated groups.

4. A Fracturing Fluid of claim 3, wherein the groups R_1 and R_2 contain 1-2 hydrophilic moieties selected from Hydroxy1 (-OH), ethoxy or propoxy.

5. The fracturing fluid of claim 1 or 2, wherein said alcohol is selected from the group consisting of benzyl alcohol, decanol, dodecanol or hexadecanol.

6. The fracturing fluid of any of claims 1 to 5, wherein said aqueous medium is selected from the group consisting of water, an aqueous solution of an inorganic salt, aqueous alkaline or acid solution, water and a lower alkanol, glycol or polyglycol and mixtures thereof.

7. The fracturing fluid of any of claims 1 to 6, wherein said alkyl group contains 14-22 carbon atoms.

8. The fracturing fluid of any of claims 1 to 6, wherein said alkyl group contains 14-24 carbon atoms and 1-2 double bonds.

9. The fracturing fluid of any of claims 1 to 6, wherein said acyl group contains 14-24 carbon atoms.

10. The fracturing fluid of any of claims 1 to 6, wherein said acyl group contains 14-24 carbon atoms and 1-2 double bonds.

11. The fracturing fluid of any of claims 1 to 8 wherein said betaine surfactant is selected from the group consisting of erucyl dimethyl betaine, docosyl dimethyl betaine, octadecyl dimethyl betaine cetyl dimethyl betaine, and tallow dimenthyl betaine and myristyl dimethyl betaine.

12. The fracturing fluid of claim 1 or 2, wherein said aqueous medium is a solution of KCl in water, said betaine surfactant is octadecyl dimethyl betaine and said alcohol is hexadecanol.

13. The fracturing fluid of claim 1 or 2, wherein said aqueous medium is a solution of KCl in water, said betaine surfactant is octadecyl dimethyl betaine and said alcohol is tetradecanol.

14. The fracturing fluid of claim 1 or 2, wherein said aqueous medium is a solution of KCl in water, said betaine surfactant is octadecyl dimethyl betaine and said alcohol is decanol.

15. The fracturing fluid of claim 1 or 2, wherein said aqueous medium is a solution of KCl in water, said betaine surfactant is octadecyl dimethyl betaine and said alcohol is benzyl alcohol.

16. The fracturing fluid of claim 1 or 2, wherein said aqueous medium is a solution of KCl in water, said betaine surfactant is hexadecyl dimethyl betaine and said alcohol is benzyl alcohol.

17. A method of fracturing subterranean formation comprising the step of injecting the fracturing fluid of claims 1 to 16 into the formation at a pressure sufficient to initiate fracturing.